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Revised values of the bond-valence parameters for Te^{IV}—O, Te^{VI}—O and Te^{IV}—Cl

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Bond-valence parameters r_0 and b have been re-determined for Te^{IV}—O: r_0 = 1.9605 Å, b = 0.41; Te^{VI}—O: r_0 = 1.921 Å, b = 0.56; and Te^{IV}—Cl: r_0 = 2.3115 Å, b = 0.555. Bond distance data from 208 independent Te^{IV}—O polyhedra, 118 Te^{VI}—O polyhedra and 26 Te^{IV}—Cl polyhedra were used, and all neighbours out to 3.5 Å were included. Root-mean square deviations of bond-valence sums on Te from ideal values were 0.1934, 0.1939 and 0.0865 v.u. The good fit for Te^{IV}—O over a range of Te coordination numbers from 3 to 12 demonstrates that there is no essential difference in character between short 'primary' Te—O bonds, oriented away from the Te lone pair, and longer 'secondary' Te—O bonds on the same side of the Te atom as the lone pair. Comparison of bond-valence sums for Te—O polyhedra obtained using the new parameters with those calculated using earlier literature values shows that the new parameters give a narrower spread of calculated bond-valence sums, which means much closer to the formal valence for both oxidation states of tellurium.

1. Introduction

The bond-valence model is a powerful and straightforward description of acid–base bonding which is used to interpret and predict the bond lengths found in crystalline solids. An in-depth discussion of the history of the method and its applications can be found in Brown (2002). The model can be used to determine bond valences, s_{ij}, which are calculated from the bond lengths, r_{ij}, using the correlation function

$$s_{ij} = \exp[(r_0 - r_{ij})/b] \quad (1)$$

where r_0 and b are the empirical parameters which are chosen such that the sums of the bond valences around the ions are the same as their formal valences (Brown, 2002). Parameters r_0 and b can be determined from well defined and constrained crystal structures. Unlike r_0, b is difficult to fit robustly, and a 'universal constant' value b = 0.37 Å is usually adopted (*e.g.* Brown & Altermatt, 1985; Brese & O'Keeffe, 1991; Brown, 2002). Over the past several years many authors have begun to recalculate r_0 and b for heavier cations. Full r_0–b fits have been undertaken for Pb^{II} (Krivovichev & Brown, 2001), U^{VI} (Burns *et al.*, 1997), Tl^{I} (Locock & Burns, 2004), Sb^{III} and Sb^{V} (Palenik *et al.*, 2005; Sidey *et al.*, 2008; Sidey, 2009; Mills *et al.*, 2009), while Sidey (2006, 2009) also re-determined the parameters for the Bi^{III}/Br^{I-} and the Sn^{II}, Sb^{III}, Te^{IV} and I^{V}/O^{II-} ion pairs. Adams (2001) refined the pairs for several alkali halides and chalcogenides and more recently, Krivovichev (2012) re-determined the r_0–b fits for Cu^{II}, Pb^{II}, Hg^{II}, Bi^{III}, Sb^{III}, Y^{III}, La^{III} and Nd^{III}.

Our interest in recalculating r_0 and b for Te^{IV} and Te^{VI} has come about from our work on new secondary Te minerals

from Otto Mountain, California (Housley *et al.*, 2011), which have yielded a number of interesting and new crystal structure types. Bond-valence sums (BVS) for Te^{IV} were consistently high ($\sim$ 4.1 v.u.), and for Te^{VI} were consistently low (5.6–5.9 v.u.) in these structures when using the parameters of Brese & O'Keeffe (1991). Kampf & Mills (2011) recently noted the need for a re-evaluation of r_0 and b for Te—O bonds with Te in both oxidation states, analogous to the recalibration which we have recently done for Sb—O (Mills *et al.*, 2009). One structure of current interest to us (rodalquilarite; Kampf & Mills, 2011) also shows weak bonding between Te^{IV} and Cl. Hence, we have also refined parameters for Te—Cl, so as to be able to calculate bond-valence sums for rodalquilarite and other compounds with Te—Cl interactions. Te^{VI} does not form compounds with chlorine.

2. Methodology and results

To obtain full r_0–b fits for Te^{IV}—O, Te^{VI}—O and Te^{IV}—Cl we employed a strict set of criteria when selecting structures from the Inorganic Crystal Structure Database, which would minimize the errors associated with calculating the new bond-valence parameters. These criteria are outlined in detail in Mills *et al.* (2009). The new mineral telluroperite, $Pb_3TeO_4Cl_2$, is a good example of a compound which was excluded from our selection, on the grounds that it shows substitution of Pb^{II} for Te^{IV}, and bonding from Te to more than one type of anion (Kampf *et al.*, 2010*f*). We have also screened out non-ambient data, and additionally have rejected structures that were found to be extreme outliers in preliminary BVS fits. After this selection process, we were left with data for 208 independent Te^{IV}—O polyhedra, 118 Te^{VI}—O polyhedra and 26 Te^{IV}—Cl polyhedra.

As was the case for Sb^{V} coordination polyhedra, there were very few examples of oxygen CN $\neq$ 6 for Te^{VI}. Including all Te^{VI}—O distances out to 3.5 Å, our dataset contained two examples of TeO_5 polyhedra, four of TeO_7, seven of TeO_8 and five of TeO_{12}, but 100 for TeO_6. Similarly, all Te^{IV}—Cl polyhedra were $TeCl_6$ except for two instances of $TeCl_7$. This is in contrast to the behaviour of Te^{IV}—O, which shows a broad, multimodal distribution of coordination numbers ranging from 3 to 12 (Fig. 1), with six and eight as the most common numbers of neighbours. Therefore, we anticipated less robust fitting of b for Te^{IV} than for Te^{VI}, since a tight constraint of b requires data for a wide range of bond valences, which is facilitated by having a wide range of coordination numbers. As in Mills *et al.* (2009), the fit was conducted by calculating bond valences for trial values of r_0 and b, and the BVS on each tellurium, and adjusting r_0 for a given value of b so as to obtain the minimum root-mean-square deviation of BVS from the ideal value. This was done for a range of b values, so as to locate the global minimum deviation. In practice, our datasets were sufficient to robustly identify optimal r_0–b pairs for both Te^{IV}—O and Te^{VI}—O; it was only for the much smaller and almost exclusively six-coordinated Te^{IV}—Cl dataset that the well known problem of correlation between r_0 and b manifested itself. This is seen clearly in Fig. 2, where the root-mean-square deviation is contoured for the three fits as a function of r_0 and b.

Table 1
Bond-valence sums on Te^{VI} for recently approved new minerals.

Mineral name	Brese & O'Keeffe	This study	Reference
Agaite	5.799	5.904	Kampf *et al.*(2013*b*)
Bairdite	5.751	5.865	Kampf *et al.* (2013*c*)
Chromschieffelinite†	5.943	6.001	Kampf *et al.* (2012)
Chromschieffelinite†	5.934	5.997	Kampf *et al.* (2012)
Eckhardite	5.824	5.912	Kampf *et al.* (2013*d*)
Fuettererite	5.671	5.822	Kampf *et al.* (2013*a*)
Housleyite†	5.804	5.907	Kampf *et al.* (2010*b*)
Housleyite†	5.650	5.798	Kampf *et al.* (2010*b*)
Kuksite‡	5.888	5.968	Mills *et al.* (2010)
Kuksite‡	5.824	5.925	Mills *et al.* (2010)
Markcooperite	5.468	5.676	Kampf *et al.* (2010*d*)
Ottoite	5.713	5.837	Kampf *et al.* (2010*a*)
Paratimroseite	5.866	5.950	Kampf *et al.* (2010*e*)
Thorneite	5.754	5.873	Kampf *et al.* (2010*c*)
Timroseite	5.757	5.880	Kampf *et al.* (2010*e*)
Yafsoanite	5.840	5.936	Mills *et al.* (2010)

† Contains multiple Te^{VI} sites. ‡ Includes multiple structure refinements.

The best-fit bond-valence parameters obtained were as follows. Te^{IV}—O: r_0 = 1.9605 Å, b = 0.41, r.m.s. deviation = 0.1934 v.u.; Te^{VI}—O: r_0 = 1.921 Å, b = 0.56, r.m.s. deviation = 0.1939 v.u.; and Te^{IV}—Cl: r_0 = 2.3115 Å, b = 0.555, r.m.s. deviation = 0.0865 v.u. As for the case of Sb^{III}—O (Mills *et al.*, 2009), the very good fit obtained for a population of Te^{IV}—O polyhedra ranging from TeO_3 to TeO_{12} demonstrates that there is no qualitative difference between the shorter, stronger 'primary' bonds, usually three or four in number and oriented away from the presumed direction of the Te^{IV} lone pair, and the longer, weaker 'secondary' bonds on the same side of the Te as the lone pair.

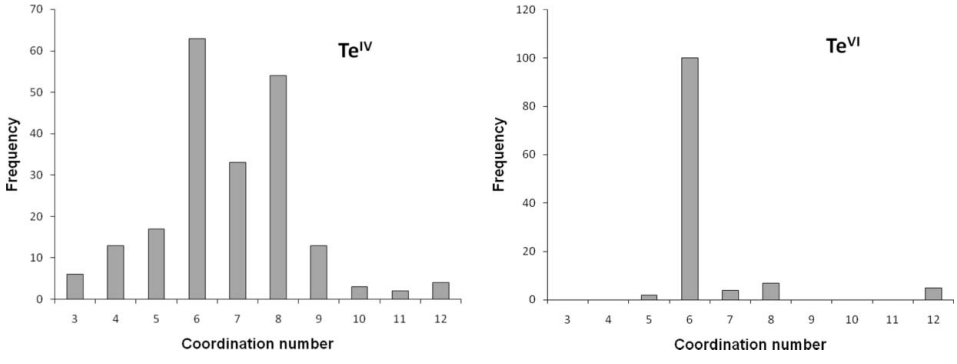

Figure 1
Distribution of coordination number n for TeO_n polyhedra of this study. Contrast the broad range of n = 3–12 for Te^{IV} with the almost exclusive n = 6 for Te^{VI}.

3. Distortion of coordination polyhedra

The geometry of oxygen coordination around tellurium is quite different for the two oxidation states, as expected. The octahedra around Te^{VI} are rather regular: bond lengths for the 100 independent $Te^{VI}O_6$ polyhedra in the dataset had a mean and standard deviation of 1.923 ± 0.041 Å. The Te^{IV}—O dataset, as noted above, may have any number between 3 and 12 oxygen neighbours within 3.5 Å of Te. Even when considering only the six-coordinated subset of Te^{IV} data for comparison with Te^{VI}, much more distortion is apparent: bond lengths for the 66 such polyhedra were 2.381 ± 0.553 Å. Much of the variance is accounted for by splitting of the six Te^{IV}—O bonds into three short and three long distances: the shortest three distances were 1.911 ± 0.077 Å, while the longest three out of the six were 2.851 ± 0.403 Å. For the full Te^{IV}—O dataset including all Te coordination numbers, the first three Te—O distances averaged 1.916 ± 0.080 Å. Using our bond-valence parameters, this implies that 3.34 v.u. out of the nominal Te valence of four are typically involved in those shortest three bonds, with any additional bonds accounting for a total of only 0.67 v.u. to Te.

The Te^{IV}—Cl data are somewhat intermediate between Te^{IV}—O and Te^{VI}—O in character. The bond distances are larger for Cl than for O, so interanion repulsion is more significant than anion–lone pair repulsion in determining the overall geometry. The coordination number was almost always 6, and for the 24 examples of $Te^{IV}Cl_6$, bond distances were 2.604 ± 0.289 Å, revealing moderate distortion of the polyhedra.

A more comprehensive way to display the distortion behaviour of $Te^{IV}O_n$ polyhedra is the bond-distance histogram of Fig. 3. This includes the full dataset of this study, with n = 3–12. It can be seen that for all polyhedra, the shortest three bond distances all have modes at 1.8–1.9 Å, while the fifth and sixth closest O atoms, if present, are most frequently at a distance close to 2.9 Å. The fourth nearest oxygen has a bimodal distribution with frequency peaks at 2.1 and 2.7 Å, indicating that some polyhedra have four short bonds rather than 3. The distortion theorem (Allmann, 1975; Brown, 1978) implies that the irregularity of $Te^{IV}O_n$ polyhedra should result in a significant increase of the mean bond distance, which might be expected to have a significant effect on the volume of the polyhedra. This was discussed briefly with regard to Sb^{III}—O polyhedra in Mills *et al.* (2009), but is explored on a more sophisticated level for our Te—O dataset in the companion paper (Christy & Mills, 2013).

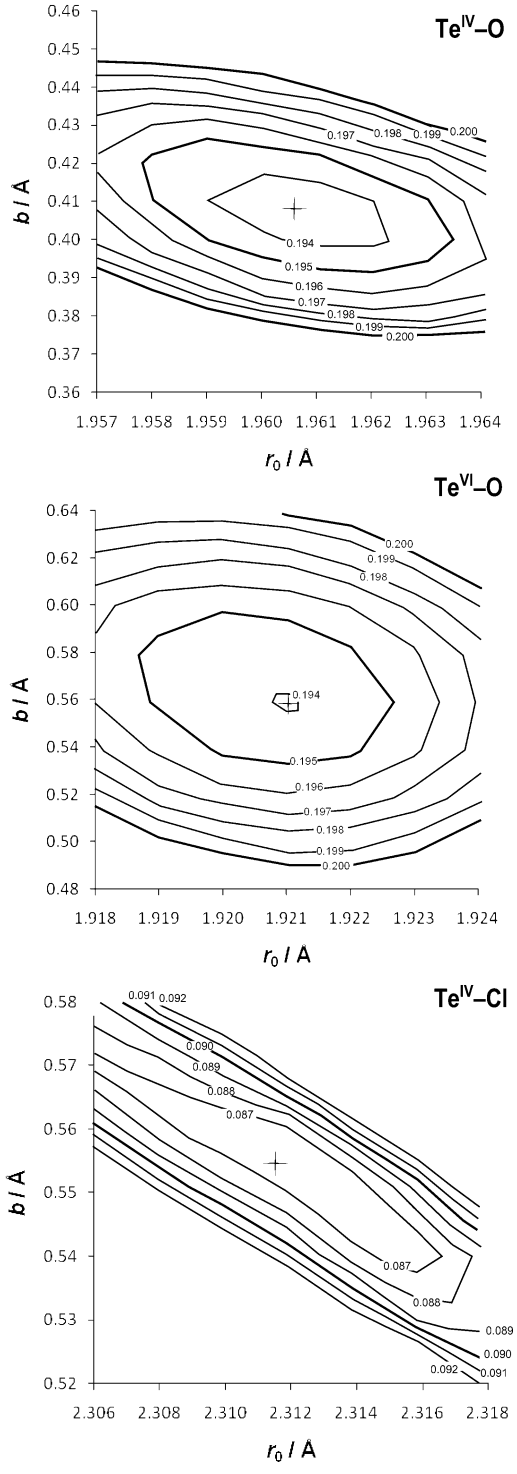

Figure 2
Contour maps of root-mean-square deviation of bond-valence sums on Te, plotted against r_0 and b for Te^{IV}—O, Te^{VI}—O and Te^{IV}—Cl. Best fit r_0–b pairs are indicated by crosses.

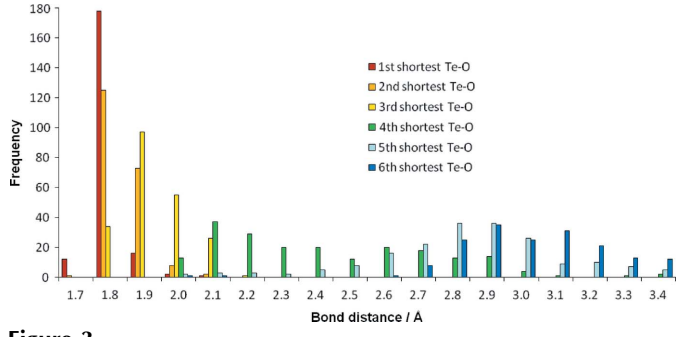

Figure 3
Distributions for $Te^{IV}O_n$ of shortest, second shortest and so on up to sixth shortest Te—O distances, where present. Bond distance bin label '1.8 Å' indicates distance in the range 1.8–1.9 Å. Bimodality between three to four short distances and remaining longer distances is apparent.

Table 2
Distribution of BVS for Te^{VI}—O and Te^{IV}—O for the full datasets of this study, calculated using our parameters, Brese & O'Keeffe (1991) and Sidey (2009).

	Te^{VI}		Te^{IV}		
	This study	Brese & O'Keeffe	This study	Brese & O'Keeffe	Sidey
Maximum	6.419	6.454	4.598	4.884	4.548
Minimum	5.146	5.172	3.006	3.144	2.960
Mean	5.997	5.915	4.003	4.160	3.980
Standard deviation	0.195	0.239	0.194	0.210	0.197
% data ± 0.1 v.u.	47.0	40.2	61.1	20.2	49.5
% data ± 0.2 v.u.	82.1	69.2	83.2	60.1	83.2

4. Comparison with other bond-valence parameterizations

For Te^{VI}—O, we have applied the new r_0 and b parameters to the 11 new tellurate minerals so far discovered at Otto Mountain, and some other Te^{VI} minerals we recently described, and compared their performance to those of Brese & O'Keeffe (1991) [r_0 = 1.917 Å, b = 0.37] (Table 1). The new parameters bring much closer to 6.0 the low BVS noted previously. When applied to the full dataset for Te^{VI}—O (Table 2), the new parameters show a smaller standard deviation than those of Brese & O'Keeffe (1991), and more of the structures have a tellurium BVS within ± 0.1 v.u. of the ideal value (47.0 *versus* 40.2%). 82.1% of the dataset lie within ± 0.2 v.u. compared with only 69.2% using the parameters of Brese & O'Keeffe (1991). The shift of the fit away from very low BVS close to 5 can be seen in the histogram of the two datasets (Fig. 4).

For Te^{IV}—O we were able to compare our new dataset with both that of Brese & O'Keeffe (1991) [r_0 = 1.977 Å, b = 0.37] and with the newer parameters derived by Sidey (2009) (r_0 = 1.955 Å, b = 0.44). In Table 2 of Sidey (2009), he shows the improved valences for a number of compounds *versus* those of Brese & O'Keeffe (1991). In Table 3 we re-analysed with our new parameters the same compounds, plus some additional structures recently solved by us. With the sole exception of K_2TeO_3, our new parameters perform the best. For our full dataset, the Brese & O'Keeffe (1991) parameters give BVS ≃ 0.1 v.u. too high, whereas the Sidey (2009) parameters over-correct and give values ≃ 0.1 v.u. too low. For Te^{IV}—O, while both our parameters and those of Sidey (2009) account for 83.2% of the total dataset within ± 0.2 v.u. of the ideal BVS (Table 2), our data puts 61.1% *versus* 49.5% of the dataset within ± 0.1 v.u. Brese & O'Keeffe (1991) parameters place only 60.1 and 20.2% within the corresponding thresholds, respectively. The difference in performance is well demonstrated in the histogram shown in Fig. 5. The new bond-valence parameters presented here for Te—O bonds are a clear improvement on those previously available. Although there are many fewer data available for comparison in the case of Te—Cl, our new parameters were obtained using the same methodology, and again are likely to be at least as good as any alternatives.

Table 3
Comparison of bond-valence sums for Te^{IV} calculated using parameters of this study with those of Brese & O'Keeffe (1991) and of Sidey (2009).

Mineral/compound name	Brese & O'Keeffe	Sidey	This study	Reference
Juabite†	4.122	3.921	3.953	Kampf & Mills (2011)
Juabite†	4.148	3.907	3.955	Kampf & Mills (2011)
Poughite†	4.120	3.900	3.940	Kampf & Mills (2011)
Poughite†	4.179	3.947	3.991	Kampf & Mills (2011)
K_2TeO_3	4.602	4.090	4.240	Andersen *et al.* (1989)
Cs_2TeO_3	4.274	3.843	3.966	Loopstra & Goubitz (1986)
$BaTeO_3$	4.179	3.837	3.926	Folger (1975)
TeO_2	4.166	4.054	4.051	Kondratyuk *et al.* (1987)
rodalquilarite‡	4.101	-	4.069	Kampf & Mills (2011)
rodalquilarite‡	4.140	-	4.125	Kampf & Mills (2011)

† Contains multiple Te^{IV} sites. ‡ Contains multiple Te^{IV} sites and Te^{IV}—Cl bonds.

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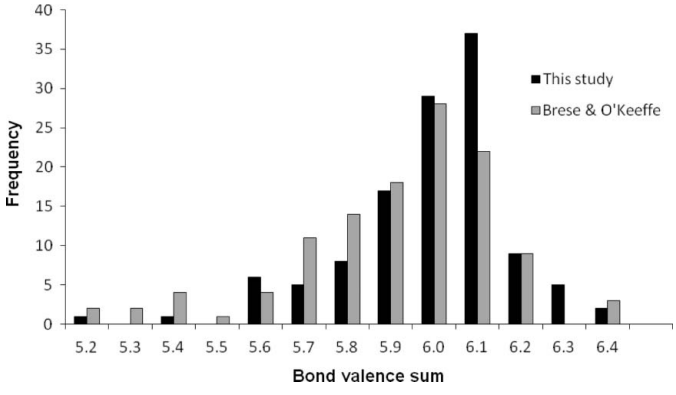

Figure 4
Comparison of distributions of bond-valence sums on Te^{VI}, calculated using our parameters and those of Brese & O'Keeffe (1991). BVS bin label '6.0 v.u.' indicates a distance in the range 5.95–6.05 v.u.

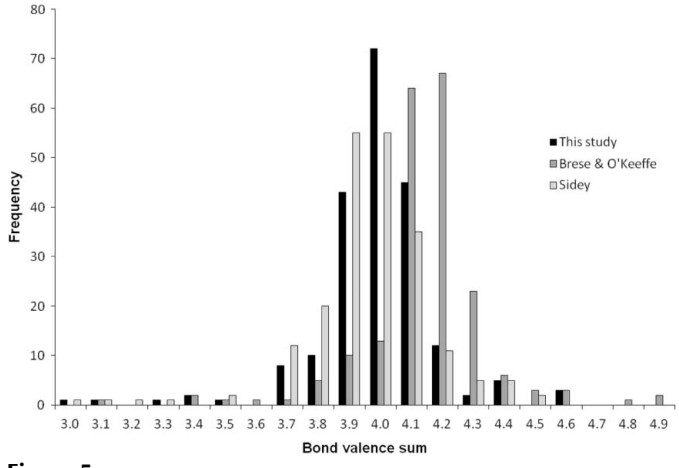

Figure 5
Comparison of distributions of bond-valence sums on Te^{IV}, calculated using our parameters and those of Brese & O'Keeffe (1991) and Sidey (2009). BVS bin label '4.0 v.u.' indicates a distance in the range 3.95–4.05 v.u.

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